Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Tetrabutylammonium 2,6-dihydroxybenzoate 2,6-dihydroxybenzoic acid solvate

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Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.005 Å
R factor = 0.043
wR factor = 0.113
Data-to-parameter ratio = 11.8

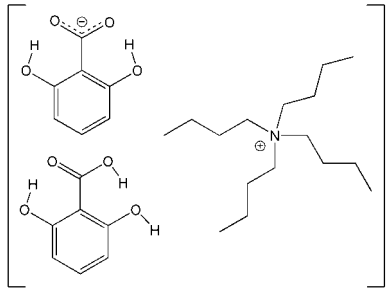
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 13 February 2003
Accepted 3 March 2003
Online 21 March 2003

The title compound, $C_{16}H_{36}N^+\cdot C_7H_5O_4^-\cdot C_7H_6O_4$ or $(^nBu_4N)^+\cdot(2,6\text{-dhb})^-\cdot(2,6\text{–Hdhb})$ [where $(^nBu_4N)$ is tetrabutylammonium, $(2,6\text{-dhb})^-$ is 2,6-dihydroxybenzoate and (2,6-Hdhb) is 2,6-dihydroxybenzoic acid], crystallizes in the space group $P1$. The crystal structure involves alternate layers, in the c direction, of cationic $[^nBu_4N]_n^{n+}$ and anionic $[(2,6\text{-dhb})(2,6\text{-Hdhb})]_n^{n-}$. Hydrogen bonds within the anionic layers form bridges between 2,6-Hdhb and 2,6-dhb$^-$ residues.

Comment

The synthesis of lanthanide complexes with appropriate organic ligands which can act as light collectors in highly luminescent novel materials is of considerable interest (Soares-Santos, Nogueira, Felix *et al.*, 2003). A literature survey shows that 2,6-dihydroxybenzoic acid (2,6-Hdhb) is an ideal candidate for such studies, since it can coordinate to several metal centres in a variety of ways, *viz*. using only the carboxylate group, in either a monodentate or bidentate-chelating mode, or through the carboxylate group along with an adjacent hydroxyl in a salicylate-type chelate. Several complexes with transition metals [Cu^{2+} (Cariati *et al.*, 1983), Co^{2+} (Erre *et al.*, 1988), Re^{5+} (Bandoli *et al.*, 1999), Pb^{2+} (Glowiak *et al.*, 1992) and Mn^{2+} (Erre *et al.*, 2000; Glowiak *et al.*, 1995)] and lanthanide ions (Glowiak *et al.*, 1999) have been reported. Several co-crystals of 2,6-Hdhb with other organic ligands have also been reported (Gdaniec *et al.*, 1994; Lynch *et al.*, 1994; Tarnura *et al.*, 1973). We describe here a co-crystal of 2,6-Hdhb with tetrabutylammonium, $(^nBu_4N)^+$, obtained in the course of our studies of lanthanide cations (Soares-Santos, Nogueira, Paz *et al.*, 2003).



(I)

The title compound, (I), crystallizes in the space group $P1$, the unit cell containing 12 independent residues [four $(^nBu_4N)^+$, four 2,6-Hdhb and four 2,6-dhb$^-$] (Fig. 1). $(^nBu_4N)^+$ cations pack in the ab plane, forming a positively charged $[^nBu_4N]_n^{n+}$ layer which alternates in the c direction with a negatively charged layer, $[(2,6\text{-dhb})(2,6\text{-Hdhb})]_n^{n-}$ (Fig. 2). However, atom O1 also acts as a bifurcated acceptor in the

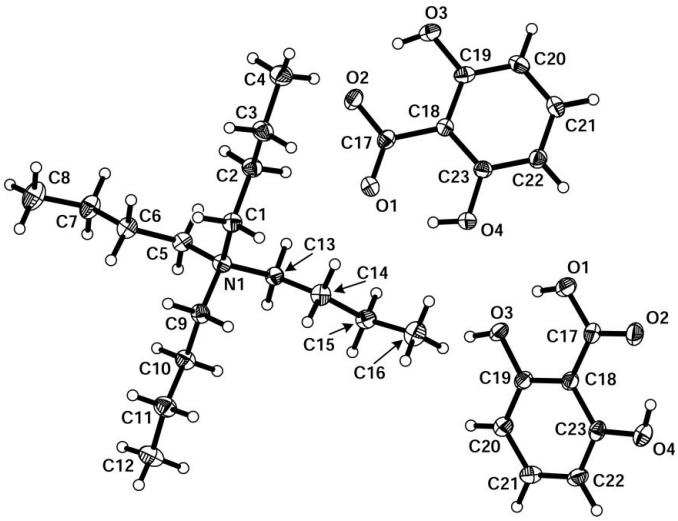


Figure 1
One quarter of the asymmetric unit of (I), showing the labelling scheme for all non-H atoms. The three depicted molecules, $[^{n}NBu_4]^+$, 2,6-dhb$^-$ and 2,6-Hdhb, correspond to the residues number 1, 8 and 12, respectively. Displacement ellipsoids are drawn at the 30% probability level.

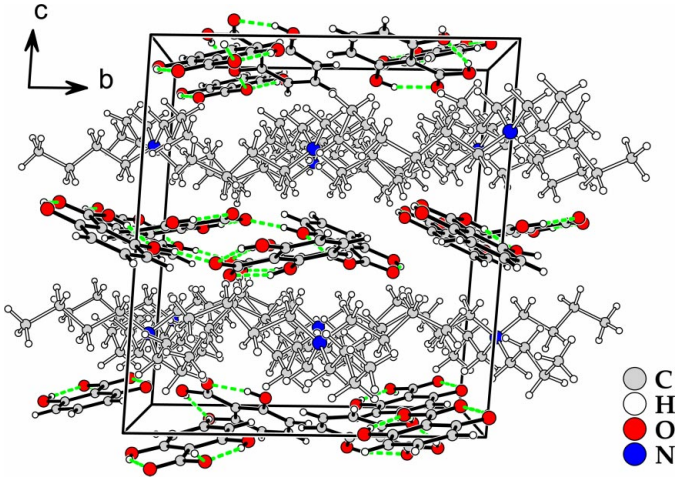


Figure 2
Perspective view of (I), showing the alternation in the *c* direction of the $[^{n}Bu_4N]_n^{n+}$ cationic layers (hollow bonds) with $[(2,6\text{-dhb})(2,6\text{-Hdhb})]_n^{n-}$ anionic layers (filled bonds). The hydrogen-bonding network is represented by green dashed lines.

hydrogen-bonding network, establishing a bridge with the neighbouring O4 atom (Fig. 3). A full listing of the hydrogen bonds is given in Table 1.

Experimental

All chemicals were supplied by Aldrich and used as received. To a solution of 2,6-dihydroxybenzoic acid (2,6-Hdhb, 0.308 g, 2.00 mmol) and KOH (0.112 g, 2.00 mmol) in distilled water (*ca* 10 ml, pH = 3), $Tb(NO_3)_3{\cdot}5H_2O$ (0.218 g, 0.50 mmol) was added and the mixture was stirred thoroughly for 1 h at ambient temperature. 5 ml of an aqueous solution containing tetrabutylammonium chloride hydrate ($^{n}Bu_4NCl{\cdot}nH_2O$, 0.556 g, 2.00 mmol) was added to the resulting

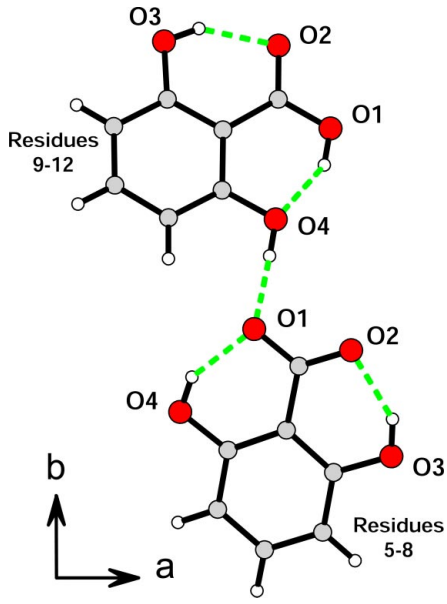


Figure 3
Detailed view of a portion of the $[(2,6\text{-dhb})(2,6\text{-Hdhb})]_n^{n-}$ and 2,6-Hdhb molecules. For hydrogen-bonding geometry and symmetry codes, see Table 1.

mixture, leading to the formation of a white flocculent precipitate. The supernatant solution was decanted and allowed to stand undisturbed at ambient temperature for about two months, after which red crystals of the title compound were manually collected.

Crystal data

$C_{16}H_{36}N^+{\cdot}C_7H_5O_4^-{\cdot}C_7H_6O_4$
M_r = 549.69
Triclinic, *P*1
a = 13.9840 (3) Å
b = 14.0507 (2) Å
c = 15.4152 (4) Å
α = 86.201 (6)°
β = 84.847 (7)°
γ = 89.898 (7)°
V = 3009.96 (11) Å^3
Z = 4
D_x = 1.213 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16891 reflections
θ = 1.0–25.0°
μ = 0.09 mm^{-1}
T = 180 (2) K
Block, red
0.23 × 0.16 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
Thin-slice ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.770, T_{max} = 0.806
26943 measured reflections
17008 independent reflections
14232 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 25.1°
h = −16 → 16
k = −16 → 16
l = −18 → 18

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.113
S = 1.12
17008 reflections
1441 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.3071P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3_5—H3_5···O2_5	0.84	1.78	2.521 (3)	147
O4_5—H4_5···O1_5	0.84	1.81	2.551 (3)	146
O3_6—H3_6···O2_6	0.84	1.78	2.535 (3)	148
O4_6—H4_6···O1_6	0.84	1.78	2.525 (3)	148
O3_7—H3_7···O2_7	0.84	1.80	2.551 (3)	147
O4_7—H4_7···O1_7	0.84	1.79	2.537 (3)	147
O3_8—H3_8···O2_8	0.84	1.77	2.525 (3)	148
O4_8—H4_8···O1_8	0.84	1.81	2.555 (3)	148
O1_9—H1_9···O4_9	0.84	1.83	2.561 (3)	145
O3_9—H3_9···O2_9	0.84	1.79	2.541 (3)	148
O4_9—H4_9···O2_8	0.84	1.70	2.534 (3)	174
O1_10—H1_10···O4_10	0.84	1.80	2.545 (3)	146
O3_10—H3_10···O2_10	0.84	1.81	2.552 (3)	147
O4_10—H4_10···O1_7^{i}	0.84	1.67	2.508 (3)	175
O1_11—H1_11···O3_11	0.84	1.80	2.558 (3)	149
O3_11—H3_11···O2_5^{ii}	0.84	1.71	2.542 (3)	173
O4_11—H4_11···O2_11	0.84	1.80	2.544 (3)	147
O1_12—H1_12···O3_12	0.84	1.79	2.545 (3)	149
O3_12—H3_12···O1_6	0.84	1.69	2.521 (3)	170
O4_12—H4_12···O2_12	0.84	1.80	2.547 (3)	147

Symmetry codes: (i) $1+x, y-1, z$; (ii) $x, 1+y, z$.

H atoms were placed in calculated positions and allowed to ride during subsequent refinement, with $U_{iso}(H) = xU_{eq}(C/O)$ ($x = 1.5$ for CH_3 and $x = 1.2$ for the remaining H atoms). Carboxylic acid groups were assigned by examining the C—O distances, with the —OH H atoms being placed using the AFIX 147 instruction in *SHELXL*97 (Sheldrick, 1997). There is a pseudo-centre at (0,0,0). As no correlation coefficients > 0.5 were found, we conclude that no change of space group is needed. This was confirmed using the ADDSYM routine in *PLATON* (Spek, 1990). Friedel data was merged before refinement and the Flack (1983) parameter was omitted since it was found to be meaningless due to the presence of a weak anomalous scatterer.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Bruker, 2001); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We are grateful to Dr John E. Davies (Cambridge) for collecting the diffraction data, to the Portuguese Foundation for Science and Technology (FCT) for financial support through PhD scholarship No. SFRH/BD/3024/2000 (to FAAP) and to the University of Aveiro for a PhD research grant (PCRSS). We also acknowledge additional financial support from FCT (grant contract POCTI/35378/QUI/2000) supported by FEDER.

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